Comment on "Raman spectroscopy study of Na_xCoO_2 and superconducting $Na_xCoO_2 \cdot yH_2O$"

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(Dated: February 6, 2008)

The effect of surface degradation of the thermolectric cobaltite on Raman spectra is discussed and compared to experimental results from Co_3O_4 single crystals. We conclude that on NaCl flux grown Na_xCoO_2 crystals a surface layer of Co_3O_4 easily forms that leads to the observation of an intense phonon around 700 cm^{-1} [Phys. Rev. B **70**, 052502 (2004)]. Raman spectra on freshly cleaved crystals from optical floating zone ovens do not show such effects and have a high frequency phonon cut-off at approximately 600 cm^{-1} [Phys. Rev. Lett **96**, 167204 (2006)]. We discuss the relation of structural dimensionality, electronic correlations and the high frequency phonon cut-off of the thermolectric cobaltite.

PACS numbers: 72.80.Ga, 75.30.-m, 71.30.+h, 78.30.-j

Raman scattering is a well established probe for structural and electronic properties of solids as, e.g. compositional and symmetry information can be gained from the number and frequency of the observed phonon modes [1]. On the other side its high surface sensitivity may also lead to challenges in sample preparation. The cobaltite $Na_xCoO_2 \cdot yH_2O$ is a correlated electron system with an enormous thermopower for large $x > 0.7$ and superconductivity for smaller $x = 1/3$ and hydration, $y = 1.3$. Due to the large mobility of Na on different sites and the mixed nominal Co valency Na_xCoO_2 has a complex defect chemistry. In the presence of CO_2 and humidity surface layers are formed that consists of, e.g. $CoCO_3$, Na_2CO_3 and Co_3O_4. The latter compound is also used as an ingot material in sample preparation [2].

The preparation of large single crystals has been reported from optical traveling floating zone (TFZ) ovens [3] and from NaCl flux (NaCl, Na_2CO_3, and B_2O_3 in varying compositions) [4]. TFZ grown crystals can easily be cleaved, while samples from NaCl flux are washed-out from the flux in water. The latter step may lead to a Na nonstoichiometry. Evidence for degradation and crystallographic changes of Na_xCoO_2 and $Na_xCoO_2 \cdot yH_2O$ on time scales from minutes to weeks exist in literature. [5, 6].

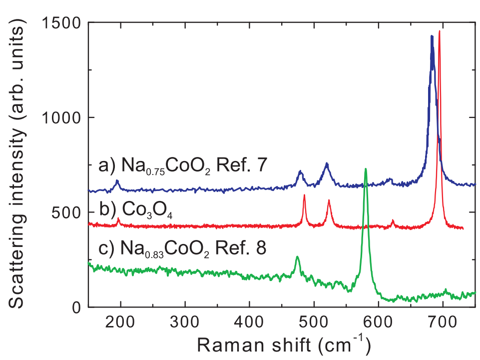

Figure 1: Raman scattering spectra of (a) NaCl flux grown $Na_{0.75}CoO_2$ at RT (Ref. 7), (b) Co_3O_4 at $T = 200$ K and (c) TFZ grown $Na_{0.83}CoO_2$ at $T = 90$ K (Ref. 8).

In a recent Raman scattering investigation of NaCl-flux grown Na_xCoO_2 crystals, Shi *et al.* have reported Raman spectra that show 5 phonons with in-plane polarization [7], see Fig. 1, curve a). These modes are attributed to five Raman active modes corresponding to displacements of sodium and oxygen [5]. In contrast to these data Raman scattering investigations on freshly cleaved TFZ grown crystals give only two modes with larger intensity [8]. These modes are attributed to oxygen in-plane and out-of-plane displacements. While the non-observance of the low frequency Na modes is attributed to disorder on the partially occupied Na sites [9], the vibrations of oxygen within the CoO_2 layers should have characteristic frequencies. Indeed a linear frequency shift of the highest frequency, out-of-plane mode at $590\,\mathrm{cm}^{-1}$ by 5% has been found with increasing Na content in the TFZ crystals [8]. The shift implies that the oxygen modes only weakly depend on the stacking of the CoO_2 layers and the occupation of Na sites that characterize the $(\alpha, \beta, \gamma$ type) crystal structure [9]. With this respect the compound can be considered as two-dimensional and the evolution of electronic correlations with doping dominates the phonon frequency [10]. Our experiments are further supported by recent inelastic X-ray scattering that show a bend over of the highest phonon branch at about $70\,\mathrm{meV} \equiv 583\,\mathrm{cm}^{-1}$ [11].

In contrast, the three-dimensional Co_3O_4 has a very intense Raman mode at a higher frequency ($690\,\mathrm{cm}^{-1}$), i.e. in the same frequency regime as Raman data [7] of NaCl-flux grown Na_xCoO_2 crystals. In Fig. 1 we show respective spectra. The small frequency shift and

broadening of curve a) compared to b) is attributed to an oxygen deficiency or a small thickness of the surface layer. Similar data on Co_3O_4 have been reported earlier by Hadjiev *et al.* [12] and more recently by Qu *et al.* discussing phase separation [13]. We conclude that the Raman data [7] of NaCl-flux grown Na_xCoO_2 are most probably interfered by a degradation of the sample leading to a surface layer of Co_3O_4. We highlight that although from symmetry analysis the same number of Raman active modes are expected, the frequency of the modes in Co_3O_4 and Na_xCoO_2 differ considerably. The intense Co_3O_4 mode at $690\,cm^{-1}$ can be used as a quality measure of cobaltates in thermoelectric applications.

Acknowledgement: We acknowledge support by the DFG within the project Le 967/4-1 and the ESF program *Highly Frustrated Magnetism.*

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[1] See, e.g. contributions to *Light Scattering in Solids*, edited by G. Güntherodt and M. Cardona (Springer, Berlin, 1984-2004).

[2] At high temperatures (T >850°C) Na_2O has a large volatility. As a result the more stable Co_3O_4 forms instead of Na_xCoO_2 with smaller or varying x. At ambient conditions the remaining Na_2O together with CO_2 and H_2O forms Na_2CO_3.

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